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The sorption of metallic ions by wood pulp during purification

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Department:

THE SORPTION OF METALLIC IONS BY WOOD PULP DURING PURIFICATION

BY

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FOREWORD

The author wishes to thank Dr. W.T. Schrenk for his advice and suggestions during the preparation of this work. The cooperation of the staff of the Cellulose Research Corporation and the use of their facilities as needed is appreciated. Indebtedness is due R.R. Boyd who proof-read and typed the manuscript throughout its preparation.

PREFACE

The study reported in this paper represents a partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering. The work was done by the author while holding the position of Graduate Assistant in the Department of Chemical Engineering and Chemistry, at the Missouri School of Mines and Metallurgy at Rolla, Missouri, with the exception of the pulping, which was done while an employee of the Cellulose Research Corporation. The assistance of members of the staff of the Cellulose Research Corporation was invaluable during the progress of the work.

INTRODUCTION

Historical review of cellulose acetate.

"Acetate" has become, within the past few years, a new member of our national vocabulary, being used to designate one of the artificial silks. (1). Like many other common-place materials, cellulose acetate has enjoyed a meteoric career. The ester made its first appearance in technical literature in 1865 when Schutzenberger (2) recorded his attempts to acetylate cellulose and other materials, and later, with Naudin (3), extended the work, the object being to determine the constitution of several of the carbohydrates. The possibilities of the acetates were

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1. "Artificial silk" is a misnomer, since the cellulose derivatives form an entirely separate class of fibers which are not related to silk.

2. Schutzenberger, P. Compt. rend. 61. 485-6 (1865) Cited by Worden, Technology of Cellulose Ethers, Vol. II, page 309.

3. Schutzenberger, P. and Naudin, Comptp rend. 68. 814 (1869) Cited by Worden Technology of Cellulose Ethers, Vol. II, page 312.

investigated by Franchimont (4,5,6,) who first introduced the use of catalysts in acetylation, thereby forming the basis of the modern art.

The first patent covering the acetylation of cellulose is accredited to Cross and Bevan (7), who in 1894 made American and British applications for a procedure using acetyl chlorine with zinc acetate as a catalyst. Worden's summary of the field since that time (8) covering the period from 1894 to 1932 requires almost 800 printed pages and includes about five thousand patents, and the literature since 1932 has probably equaled that of all the preceding years.

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4. Franchimont, A. Ber. 1879. 12. 1938. Cited by Worden, Technology of Cellulose Ethers, Vol. II, page 317.

5. Franchimont, A. Compt. rend. 1879, 89. 711. 713. 755. Cited by Worden E. Technology of Cellulose Ethers, Vol. II, page 318.

6. Franchimont, A. Compt. rend. 1881, 92, 1054, Cited by Worden, Technology of Cellulose Ethers, Vol. II, page 319

7. Cross C. & Bevan E., U.S. Pat. 530826 (1894): Brit. Pat. 9676 (1894) Cited by Worden, Technology of Cellulose Ethers, Vol. II, page 322

8. Worden, E.C., Technology of Cellulose Ethers, Newark, Newark Printing Co., 1933. Five volumes. Vol. II.

A comparative study of the products made from cellulose acetate with those of competitive materials indicates the basis of the intensive study to which it has been subjected. Cellulose acetate plastics possess high strength,. good dielectric qualities, resistance to mechanical shock, and are thermoplastic, but are more expensive than the resins and nitrocelluloses. Acetate lacquers and dopes are durable and non-inflammable, but possess low adherence for many surfaces and require comparatively high-priced solvents. Acetate rayon has high wet strength, but requires special dyeing techniques. In brief, the cost of producing cellulose acetate, and the difficulties attending its dissolving, plasticizing, and application to specific uses are problems which must be investigated before the ultimate commercial development of the material can be realized.

The price of the cellulose used as raw material for acetylation is one of the primary factors influencing the cost of the finished product. At present, cotton linters constitutes the chief practical souce of acetate, being almost pure alpha-cellulose, and cheaper than staple cotton, our other source of high alpha-cellulose. Wood pulp is the only other material offering promise as a substitute for cotton, though esparto (9),

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9. Hirst, E. Rept. Brit. Assoc. Adv. Sci., 1922. 358. Cited by Worden, Technology of Cellulose Ethers, Vol. II,545.

hemp (10) and even pine wood (11) have been suggested at various times, and wood pulp offers little competition to cotton as yet.

Many problems must be solved before wood pulp of uniform quality and sufficiently low production cost can be marketed at a lower price than cotton. While wood itself is cheap and readily delignified by the methods common to the paper industry, subsequent purification to give acetylable cellulose has proven to be difficult and is a research project of primary importance to the wood pulp industries.

Statement of the problem.

The phase of wood pulp purification selected for study was the purity of the water supply used in the manufacture of acetylable wood pulp. The importance of such knowledge is obvious on consideration of the volume of water required, a conservative estimate for production practice being one hundred and twenty gallons per pound of finished pulp. Practically no information is available concerning the effect of either the cation or anion constituents of water on the quality of cellulose acetate, although the assumption that the anions have little or no effect is justifiable at least for the sulfate ion (12).

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10. Kodak-Pathe, Fr. Pat. 728725 (1932). Cited by Worden, Tech. of Cellulose Ethers, Vol. II, p. 1060.

11. Fuchs, W. Ber. 61, 948 (1928). Cited by Worden, Tech. of Cellulose Ethers, Vol. II, page 647.

12. Water used at the plant of the Cellulose Research Corp., contains over 200 ppm total solids, largely sodium sulphate.

In regard to the cations, the practice of holding calcium, iron and manganese to a minimum has been borrowed from the textile industries, with results obtained in operation as illustrated by the following quotation (13).

"..... We have found that iron higher than one-tenth part per million (in wash water) gives definitely colored dopes. The total iron in the finished cellulose should never exceed ten parts per million and it is preferably held to five parts per million or less.

"..... Copper in the finished cellulose is bad and cannot be permitted.

" ..... All we can now give you in the way of limits of certain impurities are the indications growing out of our past experience. We do know that copper is definitely bad and that iron must be held to a low point, and that calcium and other impurities must not exceed the limit for ash set out above."

An effort has been made to fix the permissible limits of iron, copper, and manganese in the wash water used in the purification of a given type of pulp by purifying samples of a raw pulp, varying the metallic-ion content of the water used in succeeding purifications. The sorption of the metallic ions from the water was determined by analysis of ash from the finished pulps. The acetylation characteristics were determined by forming the ace-

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13. Tennesse Eastman Corp., Private Communication to F.G. Erskine, August, 1934.

tate derivative and comparing it with empirical standards.

Review of The Chemistry Involved.

Wood is an extremely complicated substance, both in its chemical constitution and physical structure, and a complete survey of the reactions occurring in the production of cellulose acetate from wood is beyond the scope of this paper. Essentially, the process involves the isolation of alpha-cellulose from wood, and the production of an acetate derivative from the cellulose. For manufacture of acetate it is necessary to remove practically all of the impurities, preferably to above 98% alpha-cellulose, without undue degradation (14) of the cellulose molecule.

In practice, the problem divides itself into three processes: 1. Digestion of the wood, 2. Purification of the crude (raw) pulp, and 3. Acetylation of the alpha-cellulose. A brief survey of the changes occurring during each of the steps is necessary in a study of the effects of the sorption during the second, and is presented only in sufficient detail to correlate the results obtained with the process as a whole.

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14. "Degradation" refers to any changes in the cellulose molecule caused by too-drastic treatment. The chief indications of degradation are lower viscosity in cuprammonium solution and increased soda-solubility. The effect may be due to rupture of the structural bonds, or due to hydrolysis of the molecule.
Hawley, L.F. & Wise, L.E., The Chemistry of Wood, 1926, page 27

1. Digestion. The wood used as a raw material was black gum (Nyssa sylvatica), with a cellulose ceontent of approximately 58 per cent, and a lignin content of approximately 25 per cent(15) Pentosans, which are substances hydrolyzing to give pentoses, account for most of the remainder of the wood; due to their relative ease of hydrolysis to give soluble derivatives, no further mention of them is required. The removal of the lignin by solution, with consequent rupture of the cell walls, is the primary object of digestion. The commonly accepted view concerning the reactions during sulfite pulping is that of Cross and Engelstad (16), who offered evidence that the chief reaction of digestion was direct sulfonation, affirming the observations of Klason (17), and Lindsey and Tollens (18), who showed that the sulfur in spent liquor was present as sulfonic acid groups. The products of digestion are crude cellulose and a spent liquor containing ligno-sulfonic acid, resins, acid-soluble mineral constituents and hydrolysis

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15. The analysis of wood is base on Schorger, A.W., Chemistry of Wood andCellulose, New York, McGraw-Hill Book Co., '26. page 34.

16. Cross, C. & Engelstad, A.J., Soc. Chem. Ind. 43 (1924)page,253-7T Cited by Schorger, A.W., Chemistry of Cellulose & Wood, page 389.

17. Klasonk P. Teknisk Tids. (1893). 17. Cited by Schorger, A.W., Chem. of Wood & Cellulose, page 389.

18. Lindsey, J.B.&Tollens, B., Ann. 267(1892) page 341. Cited by Schorger, A.W., Chem. of Cellulose & Wood, page 389

products (19). Most of the sulfonic acid derivatives are removed as the calcium salts.

The pulp after removal of the cooking liquor should be defibered or easily defiberable, contain approximately 90 per cent alpha-cellulose, 5 to 8 per cent undissolved lignin, amounts of pentosans and degraded cellulose varying with the method of digestion, and have a permanganate bleachibility of 20 per cent or less.

2. Purification. The separation of the undesired constituents from the raw pulp described in the preceding paragraph involves essentially the removal of lignin and coloring materials as chlorinated derivatives, extraction of the celluloses other than alpha-cellulose with sodium hydroxide, and swelling of the cellulose fibers. Chlorination is accomplished with gaseous chlorine, chlorine water, or hypochlorite solutions, and the reaction is generally described as formation of ligno-chlorine (20) which is soluble in water. Over-chlorination must be avoided, since it results in the loss of alpha-cellulose through oxidation and hydrolysis, and has been avoided by bleaching in stages alternated with

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19. Schorger, A.W. Chemistry of Cellulose & Wood, Chaps. III & XII.

20. Cross C. & Bevan, E. Cellulose, Page 136, Longmans, Green & Co., 1918. Cited by Hawley & Wise, The Chemistry of Wood, page 234, (illegible). The Chemical Catalog Co. 1926.

alkaline treatments, each succeeding bleaching stage representing a milder treatment. The removal of carbohydrate non-cellulosic and degraded cellulosic components is effected by treatments with sodium hydroxides. The treatment is again divided into stages, largely because changes in fiber structure occurs during causticization which render the ligneous impurities less reactive. Since components removable by bleaching diminish in amount during the treatment, the solution of the carbohydrates is effected by increasing the concentration of sodium hydroxide throughout the process. Pentosans, hexoses and gamma-cellulose are removed by hot dilute treatments, and beta-cellulose by mercerization, which also exerts a gelatinizing action on the fibrous alpha-cellulose, increasing its reactivity in acetylating solutions.

It must be remembered that the desired product is, throughout the process, in the solid state in the form of fibers of colloidal structure, relatively inert chemically, but possessive of the sorption properties common to colloidal substances.

3. Acetylation. Acetylation consists of treatment of the finish-pulp with acetic anhydride, using sulfuric acid as a catalyst. As the derivative, which is substantially the triacetate, is formed, it dissolves, acetic acid being present as solvent. Essentially, the process is one of simple esterification, complicated only by the colloidal nature of the cellulose and its derivative.

Sorption of Metallic Ions by Cellulose.

The sorption (21) of metallic ions and metallic salts by cellulose has been studied extensively, especially with regard to sodium hydroxide in mercerization and aluminum salts in paper sizing. Since the colloidal chemistry of fibrous cellulose has not been fully established, no definite correlation of the results of this series of experiments with the work of previous investigators can be made. However, a summary of the sorptions of iron, copper, and manganese reported in the literature is indicative of the trend of past work.

Schonbein (22) observed that filter paper sorbed salts from solution. Copper salts spotted on the paper did not reach the edge of the spot if in dilute solution, but covered the entire wetted area from concentrated solutions.

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21. In general, cellulose technologists make no distinction between absorption, adsorption, and chemical reactions involving addition. For example, studies of the adsorption of sodium hydroxide by cellulose, made in connection with xanthation reactions refer also to the formula of the alkali-cellulose produced.

22. Schonbein, C.F., Chem. Z entr., 32, 881-884 (1861). Cited by Schorger, A.W., The Chemistry of Cellulose and Wood, New York, McGraw-Hill Book Co., 1926, page 210.

Schellens (23) observed that filter paper fixed 0.229 per cent of iron, and cotton 0.112 per cent from one per cent ferric chloride solution. Sorption was lower from 0.1 per cent solution.

The results of Kolthoff (24), who included iron, manganese, and copper in his sorption studies, led to the conclusion that the retention of the metallic ions by filter paper was due to a base-exchange reaction with the ash constituents.

No definite conclusions concerning the extent of metallic ion sorption or the effects of time of concentration contact, temperature, pH, or the type available. Even the isoelectric point at a pH of 2.7 as reported by Gavoret (25), is based on insufficient data.

In view of the many patents covering the use of iron, copper, manganese and combinations of any two of the three as catalysts in acetylation, the detrimental effects of these elements (see page 8)

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23. Schellens, W., Arch. Pharm. 243, 617-631 (1905) Cited by Schorger, A.W., The Chemistry of Cellulose and Wood, New York, McGraw-Hill Book Co., 1926, page 210.

24. Kolthoff, I.M., Pharm. Weekblad, 58, 94(1920). Citation; Ibid. page 213.

25. Gavoret, J., Adsorption of Metallic ions by cellulose, isoelectric point of cellulose, Compt. rend., 204, 1643-5 (1937).

may be questioned. Herzog (26) investigated this problem by adding known amounts of salts in solution to the dehydrated pulp cake prior to acetylation. Both iron and copper increased the haze of the acetic acid solution of the acetate, and iron gave higher color values, while copper decreased the color markedly.

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26. Herzog, M.L., Cellulose Research Corporation, Research Program D203-1 CRC-60 (1934). Not published.

Experimental Procedure.

The purpose of this investigation was originally to determine the variation in cellulose acetate properties with variation of metallic-ion content of water. To effect this aim, raw wood pulp was purified with water of varying metal-ion content, and the resulting cellulose was analyzed for its sorption of metallic ions and acetylation characteristics. The procedure is divisible into four parts: the preparation of the raw pulp ; purification of the raw pulp to alpha cellulose; ash analysis of the alpha cellulose; and acetylation of the alpha cellulose. The following section is a detailed description of the methods employed.

Preparation of the Raw Pulp(27).

Reagents: Cooking liquor was prepared from liquid sulfur dioxide and hydrated lime by injection of the sulfur dioxide into a circulation line through which a lime-water slurry was passed. Weighed amounts of lime and sulfur dioxide were used, but the final concentration was adjusted by titration (28). The liquor as used contained 4.01 per cent sulfur dioxide of which 0.89 per cent was present as calcium bisul-

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27. Boyd, H.E., Cellulose Research Corp., Res. Program D203-1CRC-160. Not published.

28. Palmrose, Technical Association papers, 18, 309(1935) Analysis of Sulfite Liquors.

fite.

The water used for liquor makeup, pulp washing, and screening had an average analysis of 220 ppm total solids, 0 ppm hardness, 0.02 ppm iron, traces of manganese and copper, and had a pH of 7.2.

Digestion: The wood charge consisted of 8500 grams of Black Gum chips, hand-picked to remove bark and knots, with a moisture content of 12 per cent. The digester was of the rotary type, steam-jacketed, and was made of Allegheny metal. After loading the chips into the digester, steam was passed through the chips at 100 ° C. for one-half hour, the liquor charge being heated to 94° C. during that time. After steaming, rotation was started, and 45 liters of the liquor was pumped into the digester. Steam was supplied to the jacket in sufficient quantity to give a temperature of 110°C. at the end of one hour and 140°C. at the end of three and one-half hours, after which the temperature was maintained at 140°C. for five hours. A pressure of 75 lbs. per sq. inch. gauge was reached two and one-half hours after addition of the liquor, and was maintained thereafter by occasional releases.

On completion of digestion, the pulp was washed to neutrality with alternate cold and hot water washes.

It was then in the form of very soft chips, which were transferred to an Allegheny metal tub and defibered by agitation with a "Lightnin" portable agitator. The defibered pulp was screened through a 0.017 inch packer screen, centrifuged, and packed in a cellulose acetate lined bag. The yield of screened pulp was 41 per cent of the dry wood weight.

Analysis of the raw pulp gave the following: alpha cellulose, 88.4 per cent (29) viscosity, 11.41 centipoises (0.6 per cent solution in Schweitzer's reagent); pentosans, 5.9 per cent and permanganate bleachibility, 16.8 per cent (30).

No attempts were made to control the sorption of metal ions during digestion and screening. A comparison of the metallic ion contents of the wood and raw pulp was made giving the following results:

	Ash	Iron	Manganese	Copper
	per cent	ppm	ppm	ppm
Chips	0.49	trace	61.	nil
Raw Pulp	0.40	20.	25	430

29. Goff, L.E., Cellulose Research Corp., T203m CRC-3 Not published.

30. Wiles, R.H. Permanganate. Number of Pulp, Technical Assoc. Papers, Series XVII, No. 1, page 146 (1934).

The decrease in ash and manganese contents probably represents the effect of the acid medium during digestion. The action of the cooking liquor would tend toward solution of the basic ash constituents, and redeposition during washing and screening is apparently negligible. The sorption of iron and copper is a factor worthy of consideration, contamination from the apparatus being self-evident. The sorption of 20 ppm of iron is not serious, and would be difficult to avoid. However, the desirability of brass which finds use in the lines and fittings for conducting sulfur dioxide and cooking liquor, is questionable, and should be investigated further, despite the removal effected by subsequent treatment.

Purification of the Raw Pulp.

Reagents: Stock sodium hydroxide solutions were prepared by saturating distilled water with technical flake caustic, and allowing the solution to settle in tightly-stoppered bottles. The concentration of the clear liquid was determined by titration of weighed samples with 0.5 N sulfuric acid, and varied from 0.38 to 0.46 gram sodium hydroxide per gram of solution. The solutions averaged 27 mg. of iron per kilogram of 100 per cent sodium hydroxide, and negligible amounts of manganese and copper; solutions for pulp treatment were made by diluting weighed amounts of the stock solution

with the water used for washing.

Chlorine water was prepared by diffusing chlorine into distilled water until a concentration of 5 to 6 grams of chlorine per liter of solution was obtained. Concentration of chlorine was determined iodimetrically by titration with 0.1 N sodium thiosulfate. The solutions analyzed 0.1 ppm copper, 0.75 ppm manganese, and a trace of iron.

Calcium hypochlorite (bleaching powder) solutions were prepared by bubbling chlorine into a hydrated lime slurry until a concentration of approximately 5 per cent of $Ca\,OCl_2$ (assumed to contain 35 per cent available chlorine) was reached. Concentration of available chlorine was determined by the method used for chlorine water analysis. The metal-ion content was 0.5 ppm iron 0.75 ppm manganese, and a trace of copper.

Stock iron solution: 0.497 grams, $FeSO_4.7H_2O$, Baker and Adamson C.P. grade, was dissolved in distilled water containing 1 cc. of 6 N sulfuric acid and diluted to 500 cc. 1 cc. of this solution was equivalent to 1 mg. of iron.

Stock copper solution: 0.127 gram of $CuSO_4.5H_2O$, Merck's reagent grade, was dissolved in distilled water containing 1 cc. of 6 N sulfuric acid and diluted to 500 cc. 1cc. of this solution was equivalent to 0.0645 mg. of copper.

Stock manganese solution: 1.7024 grams of $MnSo_4.2H_2O$ Baker's C.P. grade, was dissolved in distilled water containing 1cc. of 6N sulfuric acid, and diluted to 500cc. 1cc. of this solution was equivalent to 1 mg. of manganese.

Distilled water was used throughout the series of purifications. The stock solutions of iron, copper, and manganese were added to give the concentration of metal ion impurities shown in Table I.

Table 1

Purification Data

Sample No.	Total Time Hours	Total Water Liters	Metallic ion in water	Ion Conc. in ppm water
W-570	168	_____	softened H_2O	
1	____	_____	None	_____
2.	____	_____	None	_____
3.	31	32.4	Fe	0.02
4.	77	32.2	Fe	0.10
5.	49	32.7	Fe	0.20
6.	71	32.6	Fe	0.40
7.	116	33.1	Cu	0.001
8.	98	32.2	Cu	0.003
9.	168	31.4	Cu	0.006
10.	51	32.4	Cu	0.010
11.	41	32.1	Mn	0.02
12.	25	31.6	Mn	0.05
13.	34	32.1	Mn	0.10
14.	39	32.0	Mn	0.20

Apparatus: Reactions were conducted in Pyrex beakers, agitating the pulp slurries with motor-driven glass agitators. Construction of the agitators with two sets of blades heavily pitched to throw upwards proved to be satisfactory. Heat was supplied by gas burners during runs 1 to 12 inclusive, and by an exposed element hotplate during runs 13 and 14. Washing was conducted in eight-inch Buchner funnels, siphoning the wash water onto the cake from graduated 14 liter bottles.

Procedure: (31). A raw pulp sample weighing 222 grams, representing 70 grams of dry material, was diluted with 2110cc. of water agitated at room temperature for 15 minutes, and washed with 2 liters of water. This step is unnecessary excepting when using a single batch of pulp for a long period of time, since it only defibers the pulp cake and removes a small amount of coloring matter.

The washed cake was weighed and treated with sufficient water and chlorine water to give a total slurry weight of 2330 grams and containing 1.895 grams of chlorine, adding the water, and the chlorine water second, with agitation. Agitation was continued for 10 minutes after adding the chlorine water, the beaker was covered

and allowed to stand at room temperature (25°C.) for an additional thirty-five minutes. Agitation was resumed, and 470 grams of solution containing 27.3 grams of 100 per cent sodium hydroxide added. The slurry was heated to boiling 100°C., boiled for 30 minutes with continuous agitation, and washed to neutrality with 3 liters of water. The chlorination and boil were, despite their continuity, two separate steps, representing the maximum delignification and the minimum caustic treatment applicable to the raw pulp. Chlorine exhaustion was complete after 30 minutes treatment, and the sodium hydroxide acted as a solvent rather than an alkaline bleaching treatment.

The washed pulp cake was weighed and treated with sufficient water and bleaching powder solution to give a slurry weight of 1900 grams and a content of 1.53 grams of $CaOCl_2$. The water and bleach were added in the same order as in chlorination, agitation again being continued for 10 minutes. The total treatment time was three hours at room temperature after which the pulp was washed to neutrality and freedom from chlorine with 3 liters of water. The effects of hypochlorite bleaching being slow, more time is required, but excess bleach is permissible.

The bleached pulp was weighed and added to sufficient sodium hydroxide solution to give a total slurry weight of 1960 grams containing 134 grams of 100 per cent sodium hydroxide, agitating during the addition. Agitation was continued, and the slurry heated to boiling (100°C.) which was maintained for three hours. Occasional addition of water was necessary to replace evaporation losses. Owing to variations in the rate of heating, the time of boiling in this step was varied between two and three hours. It recommends that the rate be controlled to require about 250cc. of makeup water during a three hour boil. At the end of three hours, the pulp was washed to neutrality with 5 liters of water.

The washed pulp was weighed and mercerized.. Sufficient sodium hydroxide solution to give 1460 grams of total slurry containing 196 grams of 100 per cent sodium hydroxide was cooled to below 25°C. The pulp cake was added to the solution in small pieces, maintaining vigorous agitation, which was continued for 15 minutes after adding the pulp. The beaker was then covered and allowed to stand for 45 minutes. Washing of the mercerized pulp was effected by diluting the slurry to approximately three and one-half liters, agitating for ten minutes, draining the liquor on the Buchner funnel, dilut-

ing to approximately two liters with water, agitating for ten minutes, and washing. The total amount of wash water used was eigh liters. The technique of mercerization is very important. Inadequate agitation permits the formation of small fiber bundles which are non-reactive in acetylating baths. The extent of mercerization varies inversely with the temperature, necessitating temperature control to within 2^{0} , the best temperature for the step as outline being 22^{0}.

The mercerized pulp cake was weighed after washing, and chlorinated. Sufficient water and chlorine water were added to give 1460 grams of total slurry containing 0.06475 grams of chlorine. The water was added first, and then the chlorine water, with agitation, which was continued for five minutes, after which the pulp was washed to neutrality and free of chlorine with three liters of water.

A final wash was applied by agitating the pulp with 1500 cc. of distilled water. The purpose of this wash was to remove non-sorbed metallic salts.

A summary of the time, reagents, and water used for each sample, given by Table II, offers an outline of the purification procedure which permits use of raw pulp samples of any weight.

Table 2.

Purification Schedule

Treatment	Amount of Reagent required	Slurry Consistency per cent dry pulp	Times, Temperature	Wash
Slurry wash	———	3.0	0.25 hours at 25°C.	To colorless
Chlorine Water Bleach	Weight Cl_2= .161 x Bleach. x Weight O.D. Pulp	3.0	0.75 hours at 25°C.	None
Sodium Hydroxide Boil	One per cent soln.	2.5	0.5 hours at 100°C.	To neutrality
$CaOCl_2$ Bleach	Weight of $CaOCl_2$= 0.03x O.D. Pulp	2.7	3.0 hours at 25°C.	Free of Cl_2
Sodium Hydroxide Boil	Seven per cent soln.	2.5	3.0 hours at 100°C.	To neutrality

Table 2 (cont.)

Treatment	Amount of Reagent Required	Slurry Consistency per cent dry pulp	Time, Temperature	Wash
Sodium Hydroxide Mercerization	13.7 per cent soln.	2.5	1.0 hour at 22°C.	To neutrality.
Chlorine Water Bleach	Weight of Cl_2 = .00175 x O.D. pulp weight	2.5	0.08 hours at 25°C.	Free of Cl_2
Distilled Water Wash	———	2.0	0.25 hours at 25°C.	With distilled water.

The scheduling of the separate steps during each purification was extremely erratic. The actual reaction time for any one batch, exclusive of preliminary and final washes and time required for heating, is 8.33 hours, and a complete purification can be run in 12 hours. A tabulation of the total purification time for each batch appears in Table I. The effect of the wide variation in time is unknown but is complicated by dust and fumes in the atmosphere, making minimization advisable. There is probably little significance in the variation in water requirements shown in Table I. Other factors which were disregarded without definite assurance that negligible effects were involved, were variations in room temperature, in rates of heating and boiling, and degree and duration of agitation. The effects of several months' storage of the raw pulp and of variations in the pH of the wash water between 5.5 and 7.4 were checked, and found to be negligible.

Each purified sample was divided into two parts, one of which was sent to the Cellulose Research Corp., for acetylation, the other being reserved for ash analysis.

Ash analysis:

Ashing:

Approximately five grams of pulp (dry basis) were dried at 105°C. and weighed in cylindrical weighing bottles. The dry pulp was transferred to porcelain crucibles, moistened, placed in a laboratory muffle at room temperature, and allowed to heat to 400°C. This temperature was maintained for two hours, or until ashing was complete, and the ashes cooled and weighed. All samples excepting 7-14 inclusive dissolved in warm 1:1 hydrochloric acid; samples 7-14 were fused with potassium bisulfate, and the fusion dissolved with water and warm 1:1 nitric acid. The solutions were diluted to 50cc. for samples to 7, and diluted to 100cc. for succeeding samples.

Iron: (32)

An aliquot representing one-fifth of the ash was oxidized with excess potassium permanganate, the excess being decolorized with hydrogen peroxide. The

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32. Thompson, H.G., Comparison of Methods for Determining small amounts of Iron, M.S.M. Thesis, 1938.

solution was diluted to 40cc., 5cc., of 1N potassium thiocyanate added, and diluted to the mark in 50 cc. Nessler tubes. Comparison was made immediately with a similarly-treated iron solution of which 1cc. was equivalent to 0.1 mg. ferric iron.

Manganese:

An aliquot representing one-fifth of the ash sample was fumed twice with 1:1 sulfuric acid and ignited if organic matter was present (present in only chlorine water sample). The residue was dissolved in 1:3 nitric acid, 0.5 grams sodium bisthmuthate added, heated to appearance of permanganate color, and decolorized while hot with sodium sulfite. The samples were cooled, excess sodium bismuthate added, stirred, filtered after five minutes, and washed and diluted to 100cc. with 1:20 sulfuric acid. Comparison was made immediately with standards prepared from solutions containing 0.01 mg. manganese per cc. as permanganic acid, simarly diluted.

Copper: (33)

An aliquot representing one-fifth of the ash sample was made slightly basic with ammonium hydroxide, al-

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33. Callan & Henderson, Determination of minute amounts of Copper with sodium diethyl dithiocarbamate, Analyst LIV, 650(1929).

lowed to stand for 15 minutes, and filtered. The filtrate was boiled almost to neutrality, cooled, placed in a 50cc. Nessler tube with 5cc. of 0.2 per cent acqueous solution of sodium diethyldithiocarbamate, diluted to the mark with water, and mixed. The yellow coloration was compared with that of standards prepared from a solution containing 0.5 mg. of copper per cc., by the same treatment used for the sample, excepting for heating and filtering, which was unnecessary.

Table 3 relates the concentrations of metallic ions in the water used with the concentrations present in the finished pulp.

Table 3

Ash Analysis

Sample No.	Iron mg/Kg pulp	Copper mg/Kg pulp	Manganese mg/Kg pulp
W-570	62	14	17
1	78		16
2	67	14	14
3	52	17	24
4	97	11	24
5	93	11	9
6	177	13	11
7	43	16	12
8	39	14	11
9	26	13	19
10	52	19	
11	35	18	14
12	68	22	20
13	49	13	16
14	31	13	44

Acetylation of finished pulp (34):

The acetylation of the finished cellulose was conducted at the laboratory of the Cellulose Research Corporation, according to the method outlined on page

The analysis of the collodions after acetylation is given in Table 4.

The cuprammonium viscosities reported with the acetylation results do not indicate any serious degradation.

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34. Olsen, F. U.S. Pat. 2,087,263, July 20, 1937.

Table 4

Acetylation Results

Sample No.	Color ppm	Haze ppm	Visc sec	Time min.	Cuprammonium Visc. 0.6% Ctp.
W-570	70	40	3		5.9
	180	50	2	115	6.0
1	500	80	1	135	7.0
2.	500	60	2	160	6.6
3	500	60	1	100	
4	500	70	1	110	5.2
5	500	70	2	120	7.9
6	500	70	2	160	8.5
7	500	60	2	110	9.5
8	500	60	1	150	
9	500	60	1	125	9.5
10	500	50	1	120	10.3
11	500	70	1	120	10.4
12	500	60	1	120	9.0
13	500	60	1	120	8.2
14	500	70	1	135	10.5

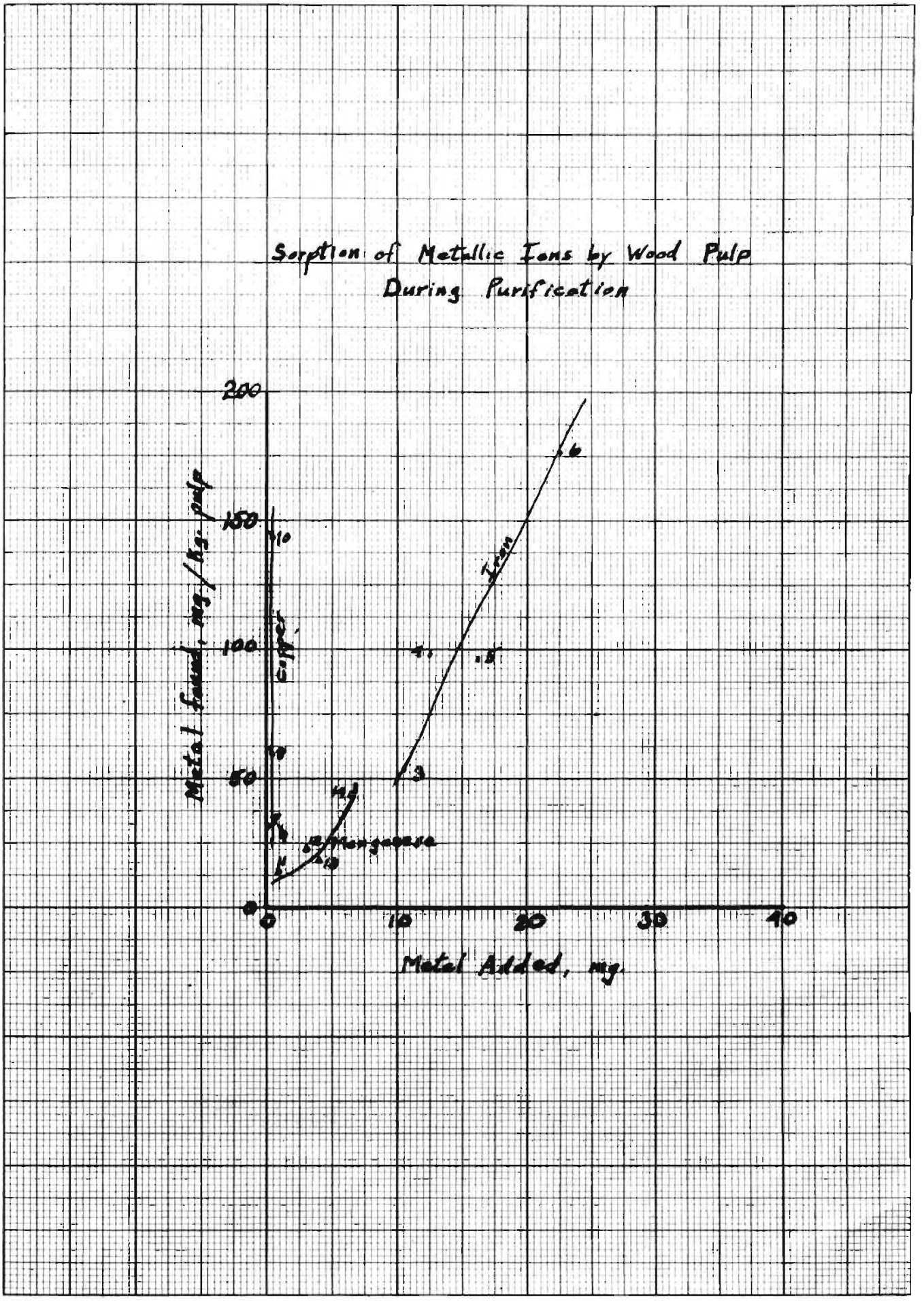
Discussion of Results.

The results of the acetylations, as given in Table 4, offer little possibility of correlation with the other data obtained. The values of color reported are beyond the range of the scale used, and are useless as determinants of the effect of previous treatment. The variations in haze and viscosity are not significant. In view of the high color values, the haze results as reported are checks. Use of a pulp of higher viscosity might have given acetate viscosities which would have served as checks on the purification procedure, but the range of 1 to 3 seconds is hardly sufficient to possess significance.

The uniformly high acetylation colors point to the presence of some contaminant in the purification reagents used during the runs at Rolla. An attempt was made to evaluate this possibility by analysis of the sodium hydroxide, bleaching powder solution, and chlorine water used, giving the values recorded on pages 20 and 21 . The high iron content of the stock sodium hydroxide solution offers sufficient basis for the abnormal colors observed.

The sorption curves for metallic ions, corrected for addition of purification reagents, are presented on page 39. The reagent corrections were applied on the basis of a single set of analyses, and cannot be considered accurate over the entire series of runs. However, the curves indicate that a correlation exists between the metallic-ion concentration of water used in

purification and the sorption by the pulp over the range of concentrations studied.


Sorption of Metallic Ions by Wood Pulp
During Purification
Metal found, mg./kg. pulp
200
150
100
50
0
Iron
Manganese
0
10
20
30
40
Metal Added, mg.

The method studied offers definite promise for commercial investigations where the selection of a water supply would depend on its effect on the product. The accumulation of sufficient data should result in the development of simpler modifications. Theoretical conclusions are unpredictable at present.

The variables during purification must be eliminated or evaluated. Among the factors to be considered are total purification time, room temperature, dust and fumes in the air, method of heating boils, method and duration of agitation, and purity of the reagents used.

Summary.

A batch of raw wood pulp has been prepared from black gum chips by sulfite digestion.

The raw pulp has been purified by a standard procedure, varying the concentration of metallic ions in the water used from sample to sample.

The purified pulp was acetylated and its acetylation characteristics determined.

The purified has been ashed and the ash analyzed for the metals studied.

A relationship has been established between the quantity of metallic in contact with the pulp during purification and the amount of metallic ion present in the finished pulp for the metals iron, copper and manganese.

Further work on the problem has been suggested, with mention of the variables worthy of consideration.

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